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OMB No. 0704-0188

1 to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering the collection of information. Send comments regarding this burden estimate or any other aspect of this form, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Avenue, Washington, DC 20543.

DATE

February 21, 1992

3. REPORT TYPE AND DATES COVERED

Final Report 8/1/90 - 12/31/91

4. TITLE AND SUBTITLE

Synthesis of Novel High Energy Density Materials
Using Nitrocarbenes

5. FUNDING NUMBERS

62302F 5730 00

6. AUTHOR(S)

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REPORT NUMBER

AFOSR-TR- 92 0207

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NC
Building 410, Bolling AFB DC
20332-6448

10. SPONSORING/MONITORING
AGENCY REPORT NUMBER

F49620-90-C-0046

11. SUPPLEMENTARY NOTES

DTIC
ELECTE
APR 8 1992
S B D

12a. DISTRIBUTION/AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The objectives of this work which were fulfilled were to 1) use high level ab initio molecular orbital theory to predict the structures and energies of potential energetic molecules and to guide the synthesis of the more promising candidate molecules, 2) synthesize a number of potential molecules and provide samples to the Astronautics Laboratory for testing, and 3) modify existing polybutadiene binders and provide samples to the Astronautics Laboratory for testing. Several novel cyclopropenes were synthesized and are considered to be good candidates for novel high energy fuels.

14. SUBJECT TERMS

Cyclopropenes, High Energy Density Materials, ab initio
calculations, Synthesis

15. NUMBER OF PAGES

9

16. PRICE CODE

17. SECURITY CLASSIFICATION
OF REPORT

UNCLASSIFIED

18. SECURITY CLASSIFICATION
OF THIS PAGE

UNCLASSIFIED

19. SECURITY CLASSIFICATION
OF ABSTRACT

UNCLASSIFIED

20. LIMITATION OF ABSTRACT

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92-08991



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Final Technical Report

SYNTHESIS OF NOVEL HIGH ENERGY DENSITY MATERIALS USING NITROCARBENES

William P. Dailey, Department of Chemistry
University of Pennsylvania, Philadelphia, PA 19104-6323

Introduction

This final technical report covers work from August 1, 1990 to December 31, 1991. It was sponsored under F49620-90-C-0046 through the Air Force Office of Scientific Research. The objectives of this work were to 1) use high level ab initio molecular orbital theory to predict the structures and energies of potential energetic molecules and to guide the synthesis of the more promising candidate molecules, 2) synthesize a number of potential molecules and provide samples to the Astronautics Laboratory for testing, and 3) modify existing polybutadiene binders and provide samples to the Astronautics Laboratory for testing. We have met all of these objectives. In addition, as a direct result of this work, we have several novel molecules under development as promising high energy fuels.

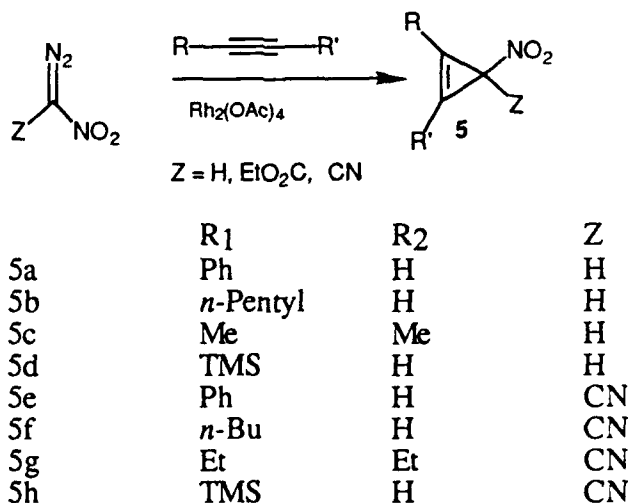
This report will be divided into several sections. The first part will concentrate on our synthetic work with nitrocyclopropenes and modification of a polybutadiene polymer with nitrocarbenes. The second section will report the results of our computational work aimed at locating promising new energetic materials. The third section will detail some of our synthetic accomplishments in the preparation of novel high energy compounds. The final section will briefly described our ongoing (and presently unfunded) research on new high energy fuels.

Synthesis of Novel High Energy Compounds using Nitrocarbenes

Over the past several years, there has been considerable interest in strained ring nitro compounds as high-energy density materials.¹ Our work in this area has focused on nitrocyclopropanes. While there are several methods for nitrocyclopropane formation,² the addition of a nitrocarbene to an alkene has only recently been described by us.³

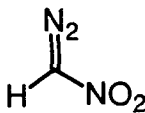
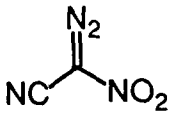
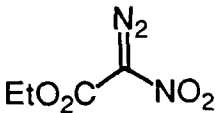
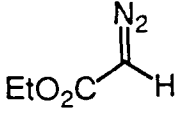
Because of the high strain energy associated with the cyclopropane skeleton (55 kcal/mol), cyclopropanes offer promise as potential energetic materials. Recently we described the formation of nitrocyclopropenes **5** from nitrodiazo compounds **1-3** and alkynes (Scheme I).⁴ These results are presented in Table 1 along with the corresponding data for ethyl diazoacetate (**4**).⁵

Scheme I



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Table 1. Yields of Cyclopropenes from Alkynes and Diazo Compounds using $\text{Rh}_2(\text{OAc})_4$.

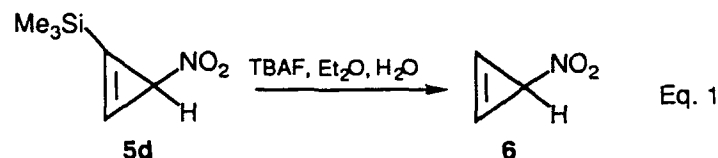
				
	1	2	3	4 ^a
PhCCH	60	65	b	0
n-ButylCCH	33 ^c	35	84	84
RCCR	35 ^d	35 ^e	0	68 ^d
TMSCCH	30	28 ^f	0	86
PhCCPh	0	0	0	-

^a Taken from ref 5. ^b Product was formed but could not be purified beyond 60% purity.

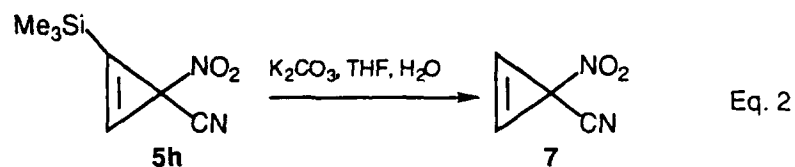
^c Reaction was carried out with 1-heptyne. ^d Reaction was carried out with 2-butyne.

^e Reaction carried out with 2-hexyne. ^f This compound was not purified but was converted directly to 3-cyano-3-nitrocyclopropene in 28% overall yield.

The parent 3-nitrocyclopropene (**6**) and 3-cyano-3-nitrocyclopropene (**7**) can be obtained from the corresponding trimethylsilyl substituted cyclopropenes **5d** and **5h**. In the case of nitrocyclopropene, deprotection with TBAF in wet diethyl ether affords a ca. 5% solution of nitrocyclopropene (Eq. 1). This material can be detected by NMR and by TLC. Our attempts to isolate **6** have been unsuccessful.

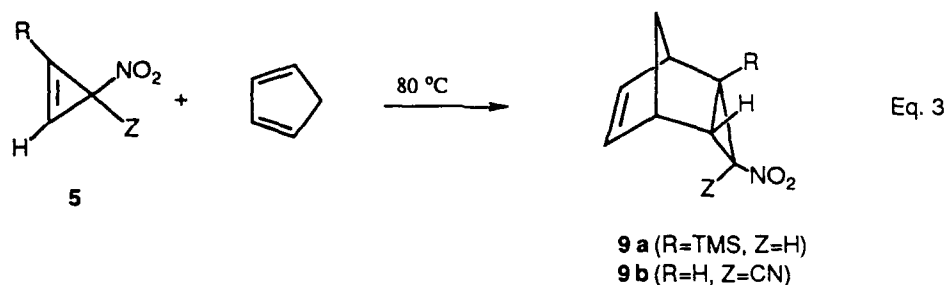


3-Cyano-3-nitrocyclopropene (**7**), on the other hand, is a relatively stable compound as a neat liquid at room temperature. It is prepared by potassium carbonate hydrolysis of the trimethylsilyl derivative **5h** (Eq 2). We prepared several grams of compound **7** and sent it to the Astronautics Laboratory for combustion testing. The results are very encouraging (I_{sp} =301 seconds with a density of 1.3 g/cc).

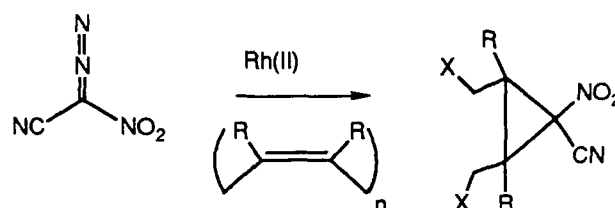


With the exception of **6**, all of these compounds are stable to air at room temperature for several days. On heating or stirring with acid they do decompose to give uncharacterizable polar materials. Nitrocyclopropenes derived from **1** solvolyze readily in hydroxylic solvents while those derived from **2** are stable to solvolysis. These compounds undergo a Diels-Alder reaction with cyclopentadiene to afford stable adducts **9** which may be fully characterized. For instance, heating nitrocyano-cyclopropene (**7**) with cyclopentadiene afforded a single isomer **9b** (Eq. 3). In this case

the stereochemistry of the adduct was determined by x-ray crystallography. As further proof of structure we have determined the crystal structure of 1-nitro-2-phenylcycloprop-2-enecarbonitrile (**5e**).

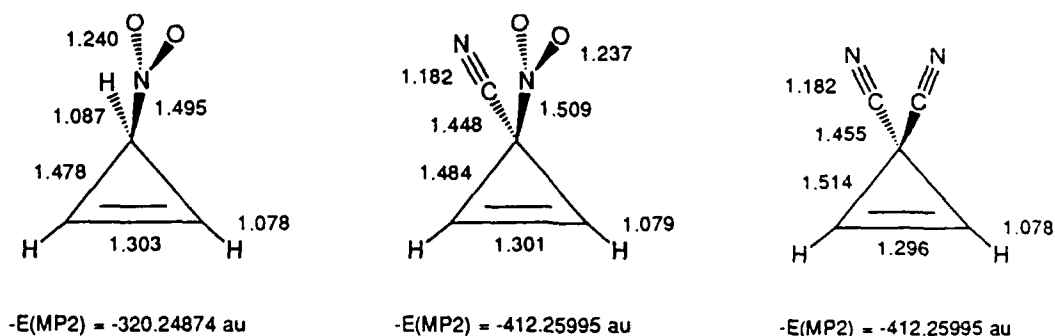


We have carried out the partial cyclopropanation of the polybutadiene propellant binder, R-45, using cyanonitrodiazomethane and catalytic rhodium acetate. If the number of cyclopropane units introduced into the polymer becomes more than about 5% of the total number of double bonds, then the polymer becomes very stiff. We sent about 5 grams of R-45 that had been converted to about 4% cyanonitrocyclopropane units to the Astronautics Laboratory for preliminary testing. So far we have not received any test results.

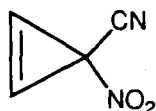


Ab initio Calculations on Potential High Energy Compounds

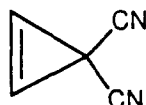
One of the objectives of this project was to locate potential high energy compounds using modern computational techniques. To begin with, *ab initio* calculations were carried out on several nitro- and cyanonitrocyclopropenes at the optimized MP2/6-31G* level. The results are shown below.



Using Schleyer's group equivalent method⁶ for converting total energies to heats of formation, we calculate $\Delta H_f^\circ = 90$ and 135 kcal/mol for 3-cyano-3-nitrocyclopropene and 3,3-dicyanocyclopropene, respectively. Both of these compounds are excellent candidates as novel high energy fuels.



$$\Delta H_f = 90 \text{ kcal/mol}$$



$$\Delta H_f = 135 \text{ kcal/mol}$$

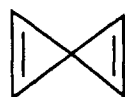
During our studies with nitrocyclopropenes, we also investigated the parent hydrocarbons to see if they would offer any advantages over the nitro substituted ones. Towards this end, we have carried out ab initio calculations at the optimized HF/6-31G* level on a range of cyclopropenes and other strained-ring compounds to derive their energies and potential as fuels. Using the Schleyer group equivalent method combined with our HF/6-31G* optimized energies gave the following predictions for heats of formation. These values were used to calculate the Isp for these compounds assuming that they would be used as monopropellants with liquid oxygen. Some of the results are shown below.



11

$$\Delta H_f = 66 \text{ kcal/mol}$$

$$I_{sp} = 326.4 \text{ sec}$$



12

$$\Delta H_f = 154 \text{ kcal/mol}$$

$$I_{sp} = 334.7 \text{ sec}$$



13

$$\Delta H_f = 99 \text{ kcal/mol}$$

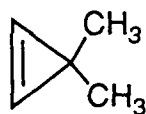
$$I_{sp} = 321.3 \text{ sec}$$



14

$$\Delta H_f = 82 \text{ kcal/mol}$$

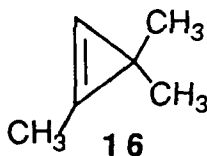
$$I_{sp} = 314.4 \text{ sec}$$



15

$$\Delta H_f = 52 \text{ kcal/mol}$$

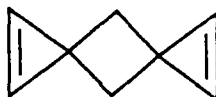
$$I_{sp} = 313.9 \text{ sec}$$



16

$$\Delta H_f = 45 \text{ kcal/mol}$$

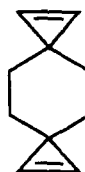
$$I_{sp} = 311.0 \text{ sec}$$



17

$$\Delta H_f = 163 \text{ kcal/mol}$$

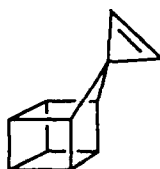
$$I_{sp} = 319.5 \text{ sec}$$



18

$$\Delta H_f = 120 \text{ kcal/mol}$$

$$I_{sp} = 310.2 \text{ sec}$$



19

$$\Delta H_f = 178 \text{ kcal/mol}$$

$$I_{sp} = 311.6 \text{ sec}$$



20

$$\Delta H_f = 184 \text{ kcal/mol}$$

$$I_{sp} = 306.3 \text{ sec}$$

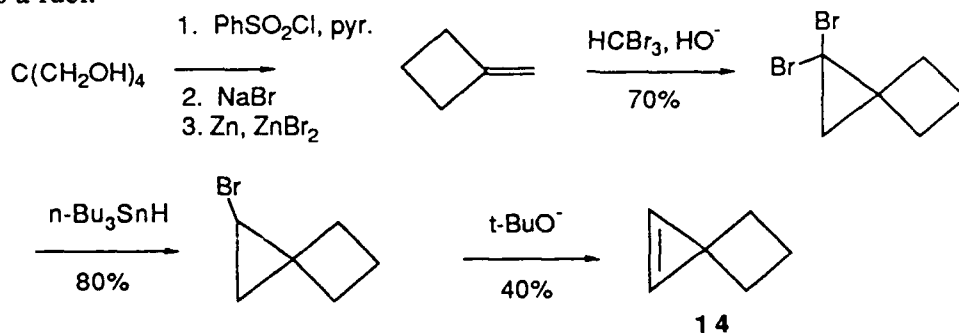
These results prompted us to modify our synthetic strategy and to focus on pure hydrocarbons. Some of the compounds we have synthesized for testing as high energy fuels by the Astronautics Laboratory are detailed in the next section. During the course of this work, a

report on the synthesis of **12** appeared.⁷ This compound, as expected, is extremely unstable. Compound **13** has also been reported and again is rather unstable.⁸

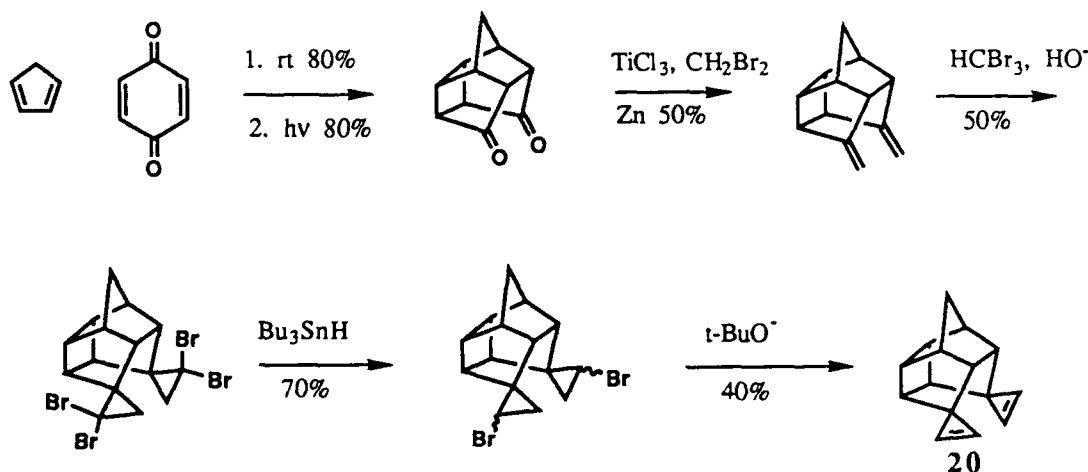
Synthesis of Novel Cyclopropenes as High Energy Fuels

Several novel cyclopropenes were prepared during the course of this work. The one feature that is most important for the stability of these systems is to have two substituents at the 3-position in the cyclopropene ring. If even one hydrogen is present in this position, the molecule undergoes a reasonably facile ene reaction with another molecule. For instance, the parent cyclopropene (**11**) is only stable below -78 °C. However as the calculations in the previous section showed, replacement of hydrogen by methyl decreases the performance of the compound.

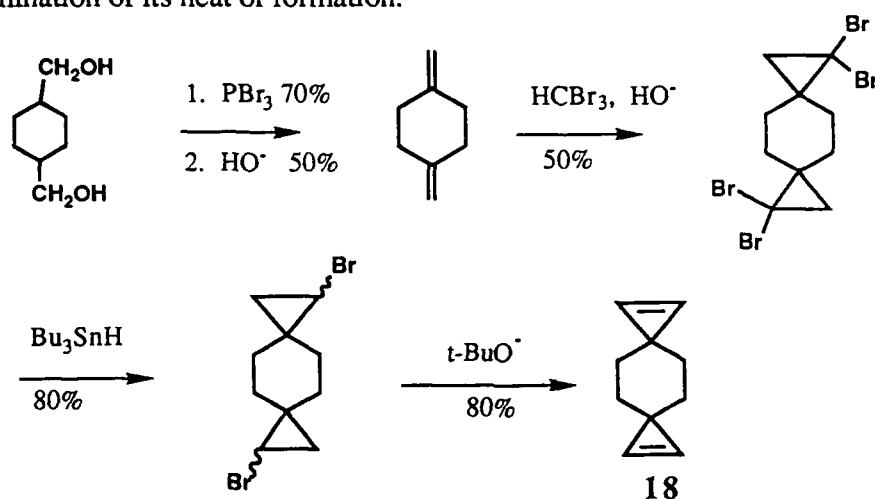
One of the first compounds that was synthesized was the spiro compound **14**. This was accomplished starting with pentaerythritol which costs \$10 per kilogram. The synthesis is shown below. While several grams of **14** were prepared, none of this material was sent to the Astronautics Lab for testing because it boils around 45 °C. Accurate combustion experiments would be very difficult on such a volatile material. However, this does not mean that it can not be used as a fuel.



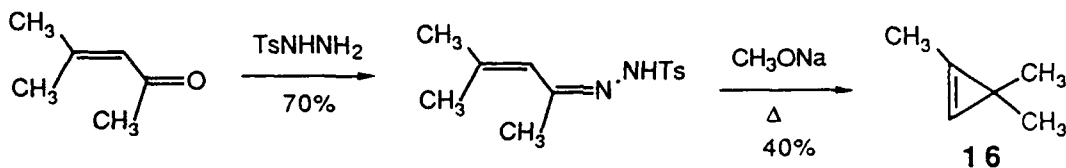
A second compound that was prepared is the caged-ring biscyclopropene **20**. Crucial to the success of this synthesis is our finding that the combination of titanium tetrachloride/methylene bromide/zinc smoothly converts the caged diketone to the bismethylene compound. The remaining steps are the same as above. Unfortunately, compound **20** is quite unstable. We believe that this is due to the edge-edge arrangement in which the two cyclopropene rings are forced. Calculations predict that the two rings are quite close to one another. Compound **20** is the first example of a compound that forces two cyclopropene units to have a strong edge-edge interaction. We plan to study reactions of this compound in the future to see how this interaction will manifest itself in novel reactivity.



Another compound that was prepared is the cyclohexane derivative **18**. Here again there is the possibility that the two cyclopropene rings would interact and cause an instability in the molecule. However, the cyclohexane ring in **18** is much more flexible than the caged structure of compound **20** and this allows the two cyclopropenes to stay far apart. The synthesis of **18** starts with the cyclohexanedimethanol which is very inexpensive (\$12 per kilo). Standard dehydration conditions yields the bismethylene compound which was taken onto compound **18** in our standard way. Compound **18** turns out to be quite stable. Several grams of compound **18** were sent to the Astronautics Laboratory for testing. Incomplete combustion and some sooting have not allowed an accurate determination of its heat of formation.



A more direct method for the formation of cyclopropenes involves the cyclization of vinyl carbenes. These reactive intermediates may be easily generated via the pyrolysis of the sodium salts of tosylhydrazones derived from enones.⁹ We used this method to prepare several grams of 1,3,3-trimethylcyclopropene (**16**). This sample was sent to the Astronautics Labs for testing. Our synthesis is shown below. This sequence can be scaled up to produce reasonable quantities of **16**. By modification of the starting enone, large quantities of 3,3-dimethylcyclopropene (**15**) can also be prepared.



Proposed Future Work

While the relative ease of synthesis of the simple cyclopropenes will allow the preparation of enough material for testing, the long term stability of these compounds could pose potential problems. The cyclopropene unit is sensitive to acid and oxygen and special precautions will be needed to ensure survivability of the samples. We have investigated other systems which will not have these problems but will still be highly energetic and relatively easy to prepare. This last point is especially important since it is one of the major reasons that cubane is not used as a fuel already. These new compounds are based on the bicyclo[1.1.1]pentane skeleton and ultimately are derived from [1.1.1]propellane (**21**). Our calculated results on these systems at the HF/6-31G* level are shown below.



21

$$\Delta H_f = 83 \text{ kcal/mol}$$

$$I_{sp} = 316.6 \text{ sec}$$



22

$$\Delta H_f = 51 \text{ kcal/mol}$$

$$I_{sp} = 313.6 \text{ sec}$$



23

$$\Delta H_f = 45 \text{ kcal/mol}$$

$$I_{sp} = 311.0 \text{ sec}$$



24

$$\Delta H_f = 95 \text{ kcal/mol}$$

$$I_{sp} = 309.9 \text{ sec}$$

[1.1.1]Propellane is easily prepared in two steps from readily available starting materials.¹⁰ As a neat liquid, **21** can survive for modest periods, but it is sensitive to acid and oxygen in the same way as the cyclopropene derivatives. However, once the central carbon-carbon bond in **21** is removed, the resulting bicyclo[1.1.1]pentane systems are extremely robust and insensitive. Compounds **22**¹¹ and **24**¹² are already known, and it should be an easy matter to prepare **23**. The added advantage to these systems, is their high symmetry which allows for high densities. Compound **24** is a solid and has a density of 1.1 g/cc. The other compounds are liquids at room temperature.

Publications and Personnel

During the course of this research effort one publication resulted. It is entitled "Synthesis of 3-Nitrocyclopropenes" by P. E. O'Bannon and W. P. Dailey and appeared in the Journal of Organic Chemistry 1991,56, 2558. Several other manuscripts are in various bntstages of preparation. These will report the synthesis and chemistry of the novel cyclopropenes **14**, **20**, and **18** along with the corresponding ab initio molecular orbital studies on these compounds.

Several different graduate students have participated in this work. Patrick O'Bannon received his Ph. D. in 1991. The title of his dissertation was "Nitrocyclopropanes from Nitrocarbenes". Two other students who also were supported by this project are Tom Golobish and Kathleen Lynch. They are both third year graduate students.

During this grant period, the PI presented portions of these results at various meetings and Universities. They included University of Iowa, Yale University, Rensselaer Polytechnic Institute, Drexel University, Wesleyan University, University of Delaware, Villanova University, University of Wisconsin, University of North Dakota, North Dakota State University, University of Minnesota, University of Florida, 201st National ACS Meeting, Swarthmore College, and Columbia University. The PI also presented work at the Annual HEDM meeting.

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